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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods
(Thirteenth session,
Geneva, 7-17 July 1997,
agenda item 4 (c))

DRAFT AMENDMENTS TO THE MANUAL OF TESTS AND CRITERIA

Other draft amendments

Additional screening procedures

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1. It is a general principle of classification that full classification tests are not performed on all the substances which are candidates for classification. Technical decisions are made on the need for particular test programmes on the basis of the physical and chemical nature of the substance, together with supplementary information from small scale screening tests. CEFIC considers that provision of example screening procedures has considerable benefits since:

- smaller quantities of materials are required for testing reducing hazards to the test personnel and adverse effects on the environment;
- it avoids unnecessary testing with consequent reduction in costs; and
- by providing consensus example procedures, a benchmark is given.

Accordingly, CEFIC submitted screening procedures (see document ST/SG/AC.10/C.3/R.672) for consideration at the 11th session of the Sub-committee.

2. The Sub-Committee recommended that further discussions be held to refine the proposals. In February 1996, CEFIC convened a meeting with invited experts from Germany, the Netherlands, Sweden and the United Kingdom. As a result of this meeting, CEFIC submitted a revised proposal (document ST/SG/AC.10/C.3/R.672/Rev.1) for consideration at the 12th session of the Sub-Committee. In order to have further technical discussions, CEFIC requested that the Energetic and Oxidizing Substances (EOS) Working Group of OECD-IGUS consider their revised proposal. The meeting was held at the Netherlands Organization for Applied Research (TNO) in May and included technical experts (acting in a personal capacity) from France, Germany, Japan, Netherlands, Norway, Sweden, United Kingdom and United States of America. As a result of this meeting, a document (INF. 10) was submitted for consideration by the Working Group on Harmonization of Classification Criteria for Reactive Substances at the 12th session of the Sub-Committee.

3. Several experts at the Working Group recognized (see document ST/SG/AC.10/C.3/24/Add.3) that the proposals were excellent from a technical point of view. The Working Group agreed that the proposals in INF. 10 were good but postponed the decision on how or where to publish. CEFIC considers that these screening procedures are best published as a new appendix to the Manual of Tests and Criteria (document ST/SG/AC.10/11/Rev.2).

4. At the last meeting of the Committee in December 1996, CEFIC presented the proposed appendix to the Manual of Tests and Criteria as INF 16 for further consideration. The progress report on criteria for physical hazards of the joint ILO/UN-Committee Working Group on Harmonised classification criteria for flammability and reactivity (document ST/SG/AC.10/R.547) endorses the development of screening procedures and recommends to publish them as a voluntary guidance to minimise the cost of testing products.

5. The technical experts of the EOS Working Group of OECD-IGUS discussed the revised proposal at their meeting at the Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology, Socorro, USA on the 10 to 14 March 1997. The ammendments suggested at this meeting have been incorporated in the proposed text.

Proposals

6. CEFIC proposes example screening procedures for:

(a) Substances which may be explosives of Class 1;

(b) Flammable liquids of Class 3;

(c) Flammable solids of Class 4;

(d) Substances which may be oxidizing substances of Class 5.

7. Proposed text for a new Appendix 6 to the Manual of Tests and Criteria is given in the annex to this document together with consequential amendments.

Annex. PROPOSED AMENDMENTS TO THE MANUAL OF TESTS AND CRITERIA (ST/SG/AC.10/11.REV.2)

GENERAL TABLE OF CONTENTS

Appendices *Insert a new entry to read:*

"Appendix 6 EXAMPLES OF SCREENING PROCEDURES"

GENERAL INTRODUCTION

1.1.2 *Append a new sentence to read:*

"In some cases, a small scale screening procedure may be used to decide whether or not it is necessary to perform larger scale classification tests. Suitable procedures are given in the introductions to some test series and in Appendix 6."

1.2.1 *Amend the last sentence to read:*

"... Test Details, on an example method for emergency relief vent sizing of portable tanks for the transport of organic peroxides and on examples of screening procedures."

INTRODUCTION TO PART II

20.3.3.3 *Amend the last indent and append a new sentence to read:*

"using rapid heating rates (differential scanning calorimetry, heating rates should normally be in the range 2 to 5 K/min.)

If differential scanning calorimetry is used, the extrapolated onset temperature is defined as being the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline."

CONTENTS OF APPENDICES

Insert a new entry to read:

"6 EXAMPLES OF SCREENING PROCEDURES"

NEW APPENDIX 6

Insert a new Appendix 6 to read:

APPENDIX 6
EXAMPLES OF SCREENING PROCEDURES

1. Purpose

1.1 Industry uses screening procedures to identify the hazard potential of raw materials, reactive mixtures and intermediates, products and by-products. The use of such procedures is essential to ensure safety during research and development and to ensure that new products and processes are as safe as possible. These procedures usually consist of a combination of a theoretical appraisal and small-scale tests and, in many cases, enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests. This reduces the quantity of material required, lessens any detrimental effect on the environment and minimizes the amount of unnecessary testing.

1.2 The purpose of this appendix is to present example screening procedures. It should be used in conjunction with any screening procedures given in the introductions to the relevant test series. With the appropriate safety margin, the results from the screening procedures adequately predict when it is not necessary to perform the classification test as a negative result would be obtained. They are presented for guidance and their use is not compulsory. Other screening procedures may be used provided that adequate correlation has been obtained with the classification tests on a representative range of substances and there is a suitable safety margin.

2. Scope

2.1 An appropriate classification procedure should be undertaken before a new product is offered for transport. If the screening procedure indicates that there is a hazard, the full classification procedure should be applied.

2.2 The screening procedures are only applicable to substances and stable, homogeneous mixtures of substances. If a mixture can separate out during transport, the screening procedure should also be performed on each reactive component of the mixture in addition to the mixture.

3. Screening procedures for substances which may be explosives of Class 1

3.1 The screening procedure may be used for new substances, not intended for explosive use, which are suspected of having explosives properties. When considering the explosive properties of self-reactive substances of Division 4.1 or organic peroxides of Division 5.2, refer to Part II of this manual and section 5.1 of this appendix. It should not be used for substances manufactured with the intention of producing a practical explosive or pyrotechnic effect.

3.2 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the material to be a potential explosive, the Class 1 Acceptance Procedure (see 10.3) should be applied.

3.3 The Class 1 Acceptance Procedure need not be applied if:

(a) There are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1

Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

or

(b) The substance contains oxygen atoms as part of oxidizing groups, e.g. chlorate, nitro etc, and the oxygen balance is less than -200. The oxygen balance is calculated for the chemical reaction:

$$C_xH_yO_z + [x + (y/4)-(z/2)].\ O_2 - x.\ CO_2 + (y/2).\ H_2O$$

using the formula:

$$\text{oxygen balance} = -1600.[2.x + (y/2) - z]/\text{molecular weight}$$

or

(c) For a single organic substance or a homogeneous mixture of organic substances, the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g.) The exothermic decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3).

Note: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than 800 J/g.

or

(d) For mixtures of inorganic oxidizing substances of Division 5.1 with organic material(s), the concentration of the inorganic oxidizing substance is:

less than 15 %, by mass, if assigned to Packing Group I (high hazard) or II (medium hazard);
less than 30 %, by mass, if assigned to Packing Group III (low hazard).

4. Screening procedures for substances which may be flammable liquids of Class 3

4.1 The procedure only applies to a mixture containing known solvents in fixed concentrations although it may contain non-volatile components e.g. polymers, additives etc. and flash points up to 110 °C. The flash point of these mixtures need not be determined experimentally if the calculated flash point of the mixture, using the method given in 4.2, is at least 5 °C greater than the relevant classification criterion and provided that:

(a) The composition of the mixture is accurately known (if the material has a specified range of composition the composition with the lowest calculated flash point should be selected for assessment);

(b) The flash point (closed cup) of each component, is known;

(c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;

(d) The considered formulation is an homogeneous mixture.

4.2 A suitable method is described by Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, **21**, 186, (1982)). For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

5. Screening procedures for substances which may be flammable solids of Class 4

5.1 *Substances which may be self-reactive substances of Division 4.1*

The classification procedures (see section 20.4) for self-reactive substances need not be applied if:

(a) There are no chemical groups associated with explosive or self-reactive properties or polymerisation present in the molecule. Examples of groups which may indicate self-reactive pro-perties are given in Table A6.2 (see Table A6.1 for chemical groups which may indicate explosive properties).

Table A6.2 EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

or

(b) For a single organic substance or a homogeneous mixture of organic substances, the onset of exothermic decomposition is greater than 175 °C or the exothermic decomposition energy is less than 300 J/g. The onset temperature and isothermal decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3).

Note: A Series A propagation of detonation test is not required if the exothermic decomposition energy is less than 800 J/g.

5.2 *Substances which may be liable to spontaneous combustion of Division 4.2*

5.2.1 The classification procedure for pyrophoric solids and liquids need not be applied when experience, in production or handling, shows that small quantities (grams) of the substance do not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

5.2.2 The classification procedure for self-heating substances need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied. Examples of screening tests are:

(a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*) with an onset temperature 80 K above the critical temperature for a volume of 1 *l*.

(b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. *Evaluation of the fire and explosion risks in drying powders,* Plant Operations Progress, **4** (3), 181 - 189, 1985) with an onset temperature 60 K above the critical temperature for a volume of 1 *l*.

5.3 *Substances which may react with water to emit flammable gases of Division 4.3*

The classification procedure for substances which may react with water to emit flammable gases need not be applied if:

(a) The chemical structure of the substance does not contain metals or metalloids; or

(b) Experience in production or handling shows that the substance does not react with water, e.g. the substance is manufactured in water or washed with water; or

(c) The substance is known to be soluble in water.

6. Screening procedures for substances which may be oxidizing substances and organic peroxides of Class 5

6.1 *Substances which may be oxidizing substances of Division 5.1*

6.1.1 For *organic compounds*, the classification procedure for oxidizing substances of Division 5.1 need not be applied if:

(a) The compound does not contain oxygen, fluorine or chlorine; or

(b) The compound contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

6.1.2 For *inorganic substances*, the test procedure in Section 34 need not be applied if the substance does not contain any oxygen or halogen atoms.

6.2 *Substances which may be organic peroxides of division 5.2*

6.2.1 Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide content of formulations (see 20.2.2).